deuterium isotope shifts (Table II).

Acknowledgment. During the course of this study, we benefited from helpful discussions with Karl Wieghardt, C. Michael Elliott, Joann Sanders-Loehr, and Thomas M. Loehr. Dr. Loehr also generously made available to us his Raman facility. Mass spectrometric measurements were made with the technical assistance of Lorne Isabelle and Bruce Tiffany. We are grateful to these individuals, and also to the U.S. Department of Energy, Office of Basic Energy Sciences, for financial support provided under Grant DE-FG06-87ER13664.

Registry No. ((bpy)$_2$Ru(OH$_2$))$_2$O^{4+}, 96364-19-1; H$_2$O, 7732-18-5; Co^{3+}, 22541-63-5.

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Synthesis and Characterization of (Tetramethylethylenediamine)(9,10-phenanthrenequinone)(9,10-phenanthrenediolato)copper(II), a Copper Complex Containing Mixed-Charge 9,10-Phenanthrenequinone Ligands

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(Tetramethylethylenediamine)(9,10-phenanthrenequinone)(9,10-phenanthrenediolato)copper(II), Cu(TMEDA)(PhenCat)(PhenBQ), has been prepared by treating copper metal with a solution containing TMEDA and 9,10-phenanthrenequinone. Dark green crystals of the complex form in the monoclinic crystal system, space group $P2_1/n$, in a unit cell of dimensions $a = 14.331$ (3) Å, $b = 11.079$ (3) Å, $c = 18.471$ (3) Å, $\beta = 101.84$ (3)°, $V = 2870$ (1) Å^3, and $Z = 4$. The coordination geometry about the copper atom is square pyramidal with TMEDA and 9,10-phenanthrenediolate ligands chelated at basal sites and the 9,10-phenanthrenequinone ligand bonded at the apical position through one oxygen atom. The diolate and quinone ligands are paired together at the metal through a charge-transfer interaction. EPR spectra of the complex recorded on solid powder samples and on a single crystal show the marked anisotropy expected of a square pyramidal complex of Cu^{2+}. Several charge distributions are possible for the complex, but this result confirms the Cu(II)–phenanthrenediolate charge distribution in the solid state.

Introduction

Much of the bioinorganic chemistry of catechols and related quinone molecules concerns interactions with copper. Direct coordination of the catecholate oxidation product of tyrosine to the binuclear dicopper center of tyrosinase has been proposed.[2] Elimination of the quinone as an oxidized benzoquinone restores the enzyme to its reduced form. Characterization on the amine oxidase enzymes has suggested that the pyrroloquinoline quinone (PQQ) redox cofactor interacts with a copper center of the enzyme.[3] It has not been shown that PQQ is actually a ligand, however. In one case, bovine plasma amine oxidase, the putative PQQ cofactor has been found to be a 6-hydroxydopa species (TOPA).[4] Evidence linking the copper center of the enzyme with the quinone may point to the existence of a Cu^{II}(Cat)/Cu^{I}(SQ) electron-transfer step in the function of the amine oxidase enzymes.[5] Bacterial phenylalanine hydroxylase contains a reduced pterin cofactor that is directly coordinated to a Cu(II) ion.[6] The reduced pterin bears an electronic similarity to an amidophenolate species. Intramolecular electron transfer may activate the metal to the Cu(I) form necessary for molecular oxygen coordination,[7] although, no direct evidence for this has been presented. The common feature of these systems is electron transfer from the reduced catecholate to the Cu(II) center with reduction of the metal to Cu(I). This is followed by addition of molecular oxygen to the reduced metal in the course of enzymatic function.

Table I. Crystallographic Data for Cu(TMEDA)(PhenCat)(PhenBQ)

mol wt	596.2	V, Å^3	2870 (1)
color	green	Z	4
cryst syst	monoclinic	D_{calcd}, g cm^{-3}	1.380
space group	$P2_1/n$	D_{exptl}, g cm^{-3}	1.38 (1)
a, Å	14.331 (3)	μ, cm^{-1}	8.0
b, Å	11.079 (3)	$T_{\max}$, $T_{\min}$	0.892, 0.903[a]
c, Å	18.471 (3)	R, R_w	0.040, 0.049
β, deg	101.84 (3)	GOF	1.28

[a] Radiation Mo Kα (0.71073 Å); T = 294–296 K. No absorption correction was applied.

Synthetic stoichiometric[8] and catalytic[9] catechol oxidation systems have been of interest, and many of these use molecular oxygen as an oxidant. In this context, studies have been carried out on catecholate complexes of copper. Early reports by Brown described copper(II) 3,5-di-*tert*-butylcatecholate complexes containing nitrogen-donor counterligands.[10] Structural studies on complexes of this type have shown that they may have monomeric, dimeric, or tetrameric structures.[11-13] Copper complexes of the 9,10-phenanthrenediolate ligand have been important as species which readily show catecholate oxidation to benzoquinone.[14] In

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Table II. Atom Coordinates (×10^4) for Cu(TMEDA)(PhenCat)(PhenBQ)

	x/a	*y/b*	*z/c*
Cu	3804 (1)	1598 (1)	2248 (1)
O1	4047 (2)	582 (3)	3115 (2)
O2	3978 (2)	146 (3)	1705 (2)
O3	5896 (2)	1664 (3)	3734 (2)
O4	5385 (2)	1831 (3)	2235 (2)
N1	3445 (3)	3051 (3)	2803 (2)
N2	3254 (3)	2540 (4)	1306 (2)
C1	4452 (3)	−415 (4)	2945 (2)
C2	4405 (3)	−656 (4)	2186 (2)
C3	4779 (3)	−1764 (4)	1961 (2)
C4	5202 (3)	−2621 (4)	2500 (3)
C5	5204 (3)	−2405 (4)	3282 (3)
C6	4816 (3)	−1311 (4)	3491 (2)
C7	4732 (3)	−2016 (5)	1209 (3)
C8	5095 (4)	−3052 (5)	992 (3)
C9	5545 (4)	−3874 (5)	1513 (3)
C10	5593 (3)	−3662 (4)	2252 (3)
C11	4775 (3)	−1128 (4)	4236 (3)
C12	5087 (4)	−1979 (5)	4763 (3)
C13	5472 (4)	−3038 (5)	4564 (3)
C14	5537 (4)	−3245 (5)	3838 (3)
C15	6207 (3)	925 (4)	3350 (3)
C16	5937 (3)	1009 (4)	2522 (2)
C17	6439 (3)	236 (4)	2080 (2)
C18	7125 (3)	−610 (4)	2419 (2)
C19	7313 (3)	−783 (4)	3233 (2)
C20	6880 (3)	−27 (4)	3672 (2)
C21	6254 (3)	369 (4)	1312 (3)
C22	6747 (4)	−267 (5)	883 (3)
C23	7439 (4)	−1069 (5)	1206 (3)
C24	7624 (3)	−1243 (4)	1967 (3)
C25	7077 (3)	−171 (5)	4443 (3)
C26	7688 (4)	−1048 (5)	4774 (3)
C27	8108 (4)	−1795 (5)	4336 (3)
C28	7931 (3)	−1674 (5)	3581 (3)
C29	2780 (5)	3765 (6)	2256 (3)
C30	3073 (6)	3782 (6)	1538 (3)
C31	2934 (4)	2691 (6)	3392 (3)
C32	4301 (4)	3713 (5)	3153 (3)
C33	3903 (4)	2581 (6)	782 (3)
C34	2370 (4)	1926 (6)	936 (3)

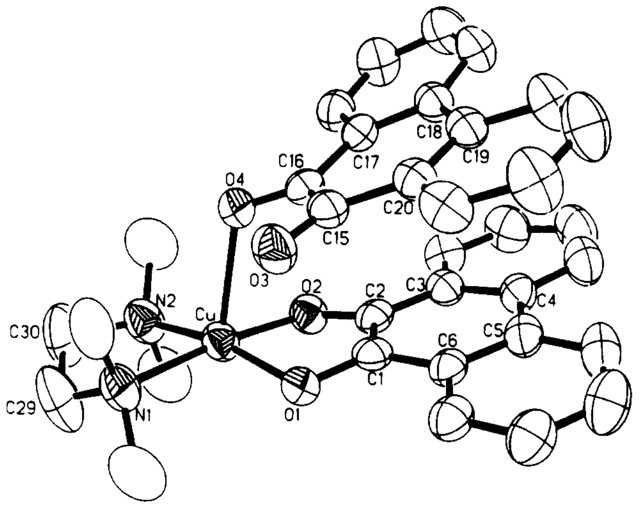

Figure 1. Plot showing the Cu(TMEDA)(PhenCat)(PhenBQ) molecule.

Table III. Bond Distances and Selected Bond Angles for Cu(TMEDA)(PhenCat)(PhenBQ)

Distances (Å)			
Cu–O1	1.929 (3)	Cu–O2	1.938 (3)
Cu–O4	2.286 (3)	Cu–N1	2.031 (4)
Cu–N2	2.044 (4)	O1–C1	1.315 (5)
O2–C2	1.316 (5)	O3–C15	1.226 (6)
O4–C16	1.250 (5)	N1–C29	1.470 (7)
N1–C31	1.486 (8)	N1–C32	1.461 (6)
N2–C30	1.480 (8)	N2–C33	1.474 (7)
N2–C34	1.476 (7)	C1–C2	1.414 (6)
C1–C6	1.436 (6)	C2–C3	1.434 (6)
C3–C4	1.419 (6)	C3–C7	1.405 (7)
C4–C5	1.464 (7)	C4–C10	1.401 (7)
C5–C6	1.419 (6)	C5–C14	1.396 (7)
C6–C11	1.403 (6)	C7–C8	1.354 (8)
C8–C9	1.385 (8)	C9–C10	1.371 (9)
C11–C12	1.363 (7)	C12–C13	1.378 (8)
C13–C14	1.381 (8)	C15–C16	1.501 (6)
C15–C20	1.470 (6)	C16–C17	1.469 (6)
C17–C18	1.409 (6)	C17–C21	1.396 (6)
C18–C19	1.484 (6)	C18–C24	1.396 (7)
C19–C20	1.397 (6)	C19–C28	1.392 (6)
C20–C25	1.402 (6)	C21–C22	1.360 (8)
C22–C23	1.373 (7)	C23–C24	1.388 (7)
C25–C26	1.366 (7)	C26–C27	1.378 (8)
C27–C28	1.371 (7)	C29–C30	1.471 (9)
Angles (deg)			
O1–Cu–O2	85.7 (1)	O1–Cu–O4	93.6 (1)
O2–Cu–O4	81.6 (1)	O1–Cu–N1	93.7 (1)
O2–Cu–N1	172.7 (1)	O4–Cu–N1	105.7 (1)
O1–Cu–N2	167.7 (1)	O2–Cu–N2	92.9 (1)
O4–Cu–N2	98.2 (1)	N1–Cu–N2	86.1 (2)

this report we describe the synthesis and characterization of (tetramethylethylenediamine)(9,10-phenanthrenediolate)(9,10-phenanthrenequinone)copper(II), a complex containing mixed-charge quinone ligands.

Experimental Section

Materials. Reagent grade chemicals were used in all experiments, and solvents were purified by standard procedures. Reactions were carried out under an atmosphere of dry argon.

Preparation of Cu(TMEDA)(PhenCat)(PhenBQ). A solution of 9,10-phenanthrenequinone (2.08 g, 10 mmol), tetramethylethylenediamine (0.82 mL, 5.5 mmol), and copper wire (5 g) in 50 mL of acetonitrile was refluxed for 20 h. After the mixture was cooled to room temperature, dark green crystals deposited. The crystals were separated from solution by filtration, washed with acetonitrile and ether, and dried in vacuum to give 1.85 g of Cu(TMEDA)(PhenCat)(PhenBQ) in 62% yield. Single crystals suitable for crystallographic characterization were obtained by recrystallization from acetonitrile.

Anal. Calcd for $C_{34}H_{32}O_4N_2Cu$: C, 68.49; H, 5.41; N, 4.70. Found: C, 68.91; H, 5.84; N, 4.90.

UV-vis: 38 800 cm^{-1} (25 600 M^{-1} cm^{-1}), 37 400 (26 900), 31 300 (5400), 24 190 (1370), 12 470 (33).

Magnetic Measurements. Room-temperature magnetic measurements were carried out on a Bruker B-E 10B8 magnetometer. The balance was calibrated with $Hg[Co(SCN)_4]$. EPR spectra were recorded on a JEOL JES-FE/3X spectrometer at X-band microwave frequency at room temperature with 100-kHz field modulation. Spectra were referenced with Mn(II)-doped MgO.

Structure Determination of Cu(TMEDA)(PhenCat)(PhenBQ). Crystals suitable for crystallographic characterization were grown from acetonitrile. A crystal resembling a dark green rhombic block was selected for data collection. Photographs taken on the crystal indicated a unit cell of monoclinic symmetry. The centered settings of 25 reflections gave the unit cell dimensions listed in Table I. Data were collected by using θ–2θ scans within the 2θ angular range 3.0–45.0°. The intensities of four standard reflections monitored during data collection showed only random fluctuations. Systematic absences were consistent with space group $P2_1/n$, a nonstandard setting of $P2_1/c$. Atom locations were determined using direct methods. Final cycles of refinement converged with discrepancy factors of $R = 0.040$ and $R_w = 0.049$. Positional parameters for all atoms of the molecule are given in Table II. Tables containing full listings of atom thermal parameters, bond lengths and angles, hydrogen atom locations, and structure factors are available as supplementary material.

Results

Description of the Cu(TMEDA)(PhenCat)(PhenBQ) Molecule. A view showing features of the Cu(TMEDA)(PhenCat)(PhenBQ) molecule is given in Figure 1; bond distances and angles are given in Table III. The coordination geometry about the metal resembles a square-based pyramid with basal sites defined by the nitrogen atoms of the TMEDA ligand and the oxygen atoms of the phenanthrenediolate ligand. The Cu atom lies 0.17 Å off the O1,O2,N1,N2 least-squares plane toward the apical oxygen. One oxygen atom of an unreduced 9,10-phenanthrenequinone is bonded

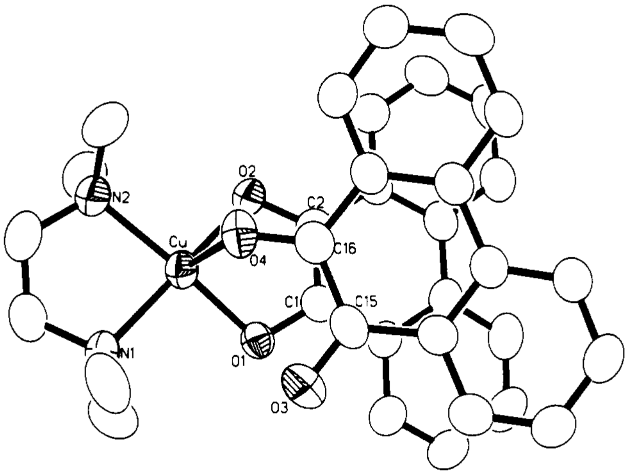

Figure 2. View of Cu(TMEDA)(PhenCat)(PhenBQ) showing the pairing interaction between PhenCat and PhenBQ ligands.

to the metal at the apical site of the pyramid. Consequently, the complex contains mixed-charge quinone ligands. A number of different charge distributions are possible for the complex, including a copper(II) form with two bonded semiquinone ligands, (TMEDA)Cu^{II}(PhenSQ)$_2$ and a copper(I) form with one semiquinone and one benzoquinone, (TMEDA)Cu^{I}(PhenSQ)(PhenBQ). In principle, the C–O lengths of the quinone ligands should provide structural information on charge distribution.[15] The phenanthrenequinone ligand bound to the metal at the apical site has C–O lengths of 1.226 (6) and 1.250 (5) Å, with the longer of the two to the coordinated oxygen atom O4. The C15–C16 bond length between carbonyl carbon atoms is essentially a single-bond value (1.501 (6) Å), and other ring C–C bond lengths agree well with values found for the unreduced 9,10-phenanthrenequinone ligand of MoO$_2$Cl$_2$(PhenBQ).[16] Structural features of the chelated quinone ligand are more puzzling. Carbonyl C–O bond lengths are 1.316 (5) and 1.317 (5) Å, intermediate between semiquinone and catecholate values. The Cu–O bond lengths to the chelated ligand are 1.929 (3) and 1.938 (3) Å. These values are intermediate between Cu–O$_{Cat}$ lengths of 1.886 (5) and 1.889 (6) Å for chelated catecholate ligands of Cu(bpy)(DBCat) and Cu(DBSQ)(DBCat)$^-$ [11,17] and average Cu–O$_{SQ}$ values of 1.957 (5), 1.937 (4), and 1.965 (6) Å for chelated semiquinone ligands of Cu(NH(py)$_2$)(DBSQ)$^+$, [Cu(DBSQ)$_2$]$_2$, and Cu(DBSQ)(DBCat)$^-$.[17-19]

The result of the crystal structure is inconclusive in pointing to a clear, localized charge distribution for the complex. Structural features of the ligands suggest that the electronic structure is between Cu^{II}(TMEDA)(PhenCat)(PhenBQ) and Cu^{I}(PhenSQ)(PhenBQ). A feature of the complex that may be significant in the analysis of the relationship between structure and charge distribution is the paired interaction between quinone ligands shown in Figure 2. Strong pairing interactions of this type have been observed previously between PhenSQ ligands of Mo$_2$O$_5$(PhenSQ)$_2$, Re$_2$(CO)$_7$(PhenSQ)$_2$, and Cu$_2$(PPh$_3$)$_2$(PhenSQ)$_2$.[20-22] In the present case, the ligands involved are of different charge and the situation is more similar to the intramolecular tetrachloro-1,2-benzoquinone–tetrachloro-1,2-semiquinone pairing in Ni(L)(Cl$_4$SQ)(Cl$_4$BQ) (L = 2,4,4-trimethyl-1,5,9-triazacyclododec-1-ene).[23] This complex was formulated as a Ni(I) species, largely on the basis of the structural features of the quinone ligands. The PhenCat and PhenBQ ligands are nearly coplanar with a dihedral angle of 17.3° between ligand planes. Closest interatomic contacts between ligands occur for the carbonyl carbon atoms with distances of 2.836 and 2.883 Å for the C2–C16 and C1–C15 separations, respectively.

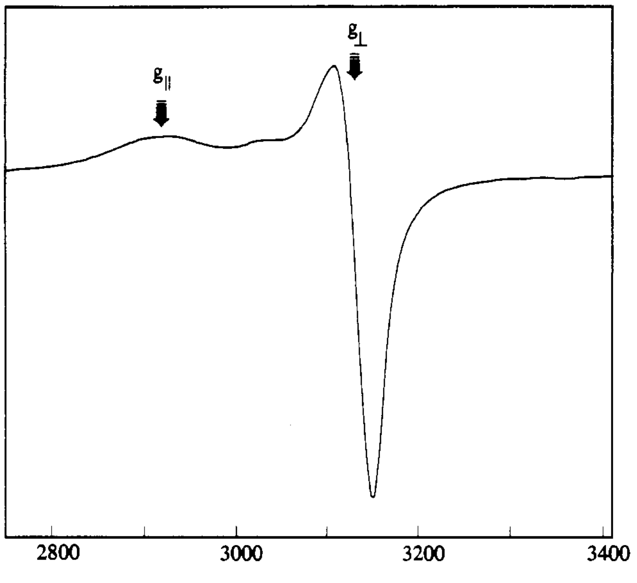

Figure 3. Solid-state powder EPR spectrum of Cu(TMEDA)(PhenCat)(PhenBQ).

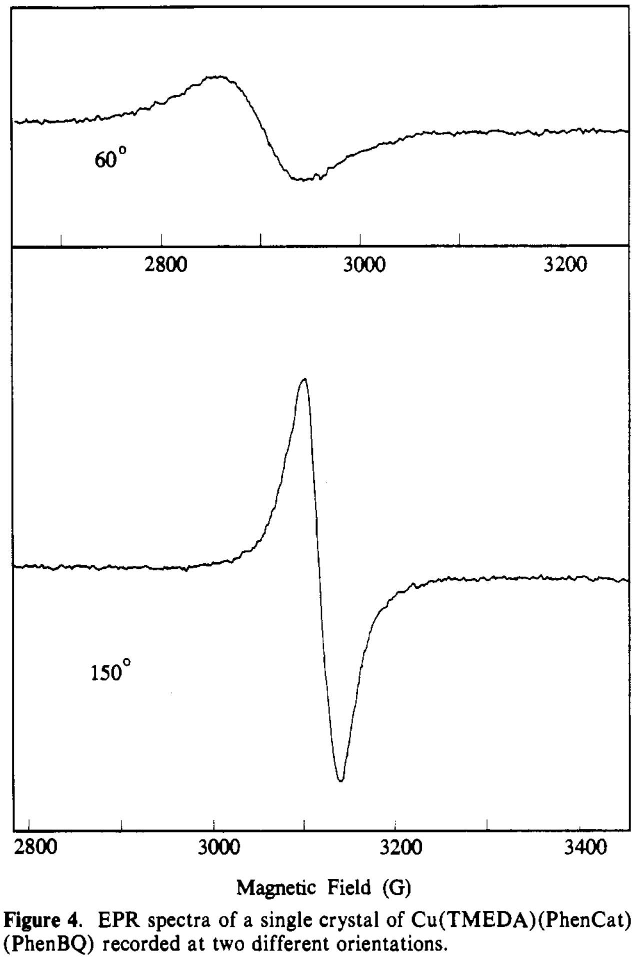

Figure 4. EPR spectra of a single crystal of Cu(TMEDA)(PhenCat)(PhenBQ) recorded at two different orientations.

EPR Spectra of Cu(TMEDA)(PhenCat)(PhenBQ). Magnetic measurements made on Cu(TMEDA)(PhenCat)(PhenBQ) gave a value of 1.9 μ_B, which is typical of $S = {}^1/_2$ Cu^{2+}. X-band EPR spectra recorded on a nonoriented powder sample of the complex show the approximate axial character given in Figure 3, with values of $g_\parallel = 2.22$ and $g_\perp = 2.065$. Single-crystal spectra consist of

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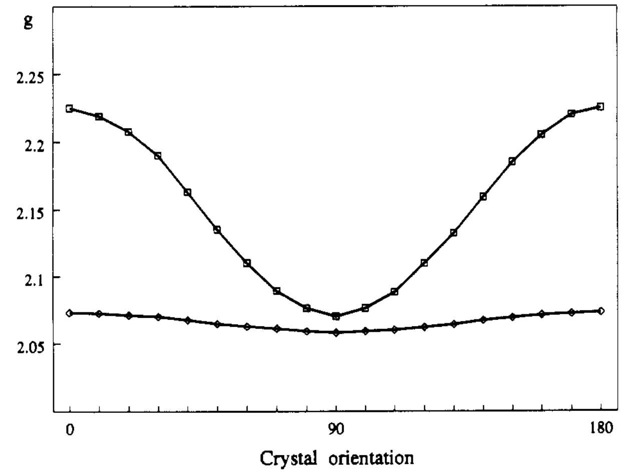

Figure 5. Variation of *g* factor with single-crystal orientation for Cu(TMEDA)(PhenCat)(PhenBQ). The upper plot corresponds to rotation about the crystallographic *c* axis with the zero angle corresponding to an orientation with field alignment normal to the *bc* plane. The lower plot corresponds to rotation about the *a** axis with the zero angle corresponding to field alignment with the *b* axis.

a single line at all orientations, as shown in Figure 4. The largest *g* factor was observed when the magnetic field was parallel to the crystallographic *a* axis, and this *g* factor agrees with $g_{\|}$ of the powder pattern. This corresponded to an orientation normal to the largest crystal face. Rotation of the crystal about the *c* axis (Figure 5) results in *g* factor variation that may be represented as $g = (g_{\|}^2 \cos^2 \theta + g_{\perp}^2 \sin^2 \theta)^{1/2}$, where θ is zero if the field is aligned with the normal to the *bc* plane, and the adjustable parameters are $g_{\|} = 2.225$ and $g_{\perp} = 2.070$. A smaller, but significant, *g* variation was observed when the crystal was rotated about the normal to the largest crystal face. This variation may be described by the equation $g = (g_1^2 \cos^2 \psi + g_2^2 \sin^2 \psi)^{1/2}$, where ψ is zero if the field is aligned with the *b* axis and $g_1 = 2.073$ and $g_2 = 2.058$.

This behavior can be explained by examination of the crystal structure of Cu(TMEDA)(PhenCat)(PhenBQ). Two adjacent complex molecules are paired by interactions between PhenBQ ligands. This creates a centrosymmetric bimolecular unit that defines the packing arrangement as shown in Figure 6. Repeating units form columns aligned along the crystallographic *a* axis. An effect of this packing arrangement is the coplanar alignment of the tetragonal planes of complex molecules in a direction perpendicular to the axis of the stack. With spin density concentrated in the tetragonal plane of the complex, magnetic anisotropy is observed to be greatest with the stacking axis aligned with the magnetic field.

Discussion

The complex that is formed initially in the synthetic procedure is Cu(TMEDA)(PhenCat). This complex together with quinone oxygenation reactions will be described separately.[24] Addition of PhenBQ to Cu(TMEDA)(PhenCat) is of interest as a potential model for the addition of molecular oxygen to the copper catecholate complex. The reduction potentials of O_2 and PhenBQ are similar, and they both may undergo two-electron reduction in sequential steps. This aspect of the oxidative addition of quinones to nucleophilic metal complexes has been noted previously.[25]

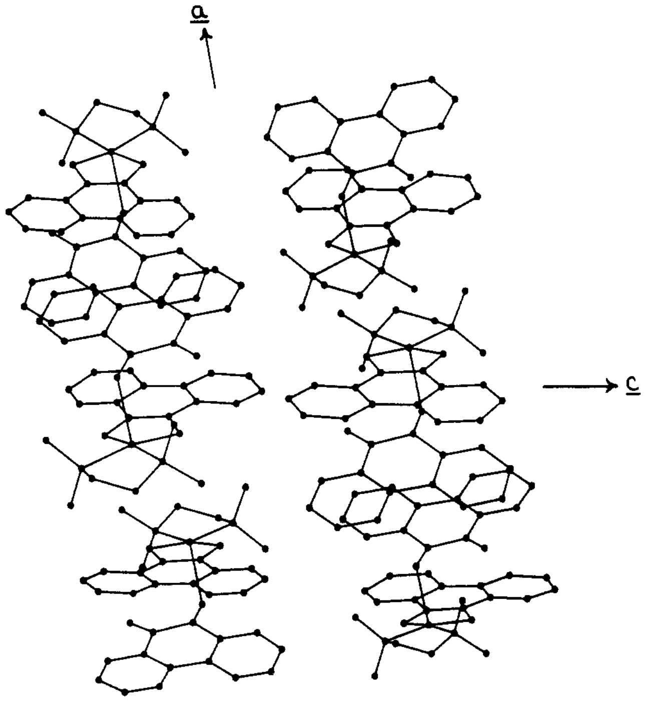

Figure 6. View of the molecular packing in the crystal structure of Cu(TMEDA)(PhenCat)(PhenBQ). The view is down the crystallographic *b* axis with *a* in the vertical direction.

The results of the EPR study on Cu(TMEDA)(PhenCat)(PhenBQ) in the solid srate clearly indicate that it contains Cu(II) and that the mixed-charge catecholate/benzoquinone charge distribution for the ligands is most appropriate. This is not completely in accord with the results of the X-ray structure. Reasons for the discrepancy are not clear but may be related to the charge-transfer pairing between ligands. Structural features of paired semiquinone ligands of $Mo_2O_5(PhenSQ)_2$, $Re_2(CO)_7(PhenSQ)_2$, and $Cu_2(PPh_3)_2(PhenSQ)_2$ appeared normal.[20-22] However, with the difference in charge between quinone ligands of Cu(TMEDA)(PhenCat)(PhenBQ), it is possible that the catecholate ligand may appear to be partially oxidized and the benzoquinone ligand partially reduced. Structural features of the quinone ligands of $Ni(L)(Cl_4SQ)(Cl_4BQ)$ also show a hint of this effect.[23] While the C–O bond lengths of the benzoquinone ligand are both 1.23 (1) Å, typically a benzoquinone value, the lengths of the semiquinone ligand are 1.25 (1) and 1.28 (1) Å, values that are shorter than typical semiquinone lengths.[15] The magnitudes of the esd's make comparisons of this type tenuous, and further high-resolution structural characterizations will be required to establish this as a general feature of complexes containing quinone ligands of differing charge.

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Supplementary Material Available: For Cu(TMEDA)(PhenCat)(PhenBQ), tables giving crystal data and information on the structure determination, atom coordinates, anisotropic thermal parameters, hydrogen atom locations, and bond distances and angles (9 pages); a listing of structure factors (10 pages). Ordering information is given on any current masthead page.

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